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THE BINDING STATE OF In AND Sn IN NATURAL SULPHIDES: FIRST RESULTS OF A COMPARATIVE STUDY BY X-RAY ABSORPTION SPECTROSCOPY AT THE *L* - EDGE *

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Problematic

One electron in the outer shell makes the difference between In and Sn, two scarce metals with ***very distinct crystal chemical behaviour*** in the Earth's crust: ***indium is clearly chalcophile***, seldom forming specific minerals and occurring mostly dispersed in excess-metal polymetallic sulphides, while ***tin is markedly lithophile.***

Indium is nowadays widely used in many technologic fields ranging from solders to high-tech devices and its consumption is expected to increase in the near future, focusing a special interest on the improvement of recycling technologies and on the exploitation of promising ***poly-metallic sulphide ores*** - e.g., the Iberian Pyrite Belt (fig.1). Despite being extracted mainly from the natural oxide (cassiterite, SnO_2), tin occurrence in sulphide ores is also economically valuable and deserves attention.

The recovery of indium stands mostly on zinc extraction from natural cubic ZnS – sphalerite, the prototype of so-called «***tetrahedral structures***» (fig.2) where the metal ions fill half of the available tetrahedral sites within a cubic closest packing of sulphur anions. This anionic array (fig.3) is particularly suitable to accommodate poly-cations within close edge-sharing tetrahedral sites [1,2], as occurs in excess-metal copper sulphides (e.g., bornite, Cu_5FeS_4), recognized to be relevant In-carrier minerals in polymetallic sulphide ore deposits. Various natural Sn sulphides (e.g., stannite, Cu_2FeSnS_4) display a similar structural situation.

The relevance of assessing the ***binding state of In & Sn in natural sulphides*** then becomes clear, and the present work describes a contribution to that problematic by using ***synchrotron radiation X-ray absorption spectroscopy.***

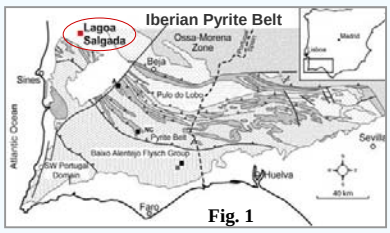


Fig. 1

Fig. 5

MAIN CRYSTAL STRUCTURE-TYPES (*STP*) adopted by NATURAL SULPHIDES

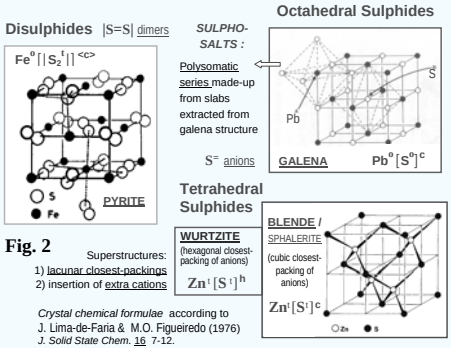


Fig. 2

Superstructures:
1) lacunar closest-packings
2) insertion of extra cations

Crystal chemical formulae according to J. Lima-de-Faria & M.O. Figueiredo (1976) *J. Solid State Chem.* 16, 7-12.

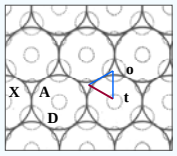


Fig. 3 - *Condensed-model* [3] *standard sheet* for $A^t_2D^o[X]^{c/h}$

Large circles, closest-packing atoms (X); A, tetrahedral (t), D, octahedral (o) interstices

Ideal radii: $r_A = 0.225\ r_X$, $r_D = 0.414\ r_X$

[t-o] & [t-t] distances are shown

Experimental

X-ray absorption experiments at **In** & **Sn** L_3-**edge** were carried out at the ***ESRF*** (European Synchrotron Radiation Facility), using the instrumental set-up of ***beamline*** **ID-21** [10,11] (fig. 5).

Polymetallic chalcogenide ores (In ~90 ppm) from Lagoa Salgada [12] (fig.6) were irradiated, along with In & Sn (*metals*) and *model compounds* displaying distinct bonding situations towards various ligands (oxygen, halides). *XANES* spectra were collected in fluorescence yield (FY) mode using a photodiode detector mounted in the horizontal plane perpendicular to the X-ray beam, and irradiating directly sample fragments with a beam-size of 1 x 0.3 μm². A fixed-exit Si(111) monochromator was used for the energy scans, assuring an *energy resolution* of 0.4 eV at the studied L_3-edges.

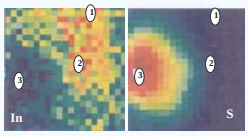


Fig. 7 - Topochemical mapping of irradiated area in sample LS 5-180.6
Red, maximum, and blue, minimum, concentration of the selected element (In or S)

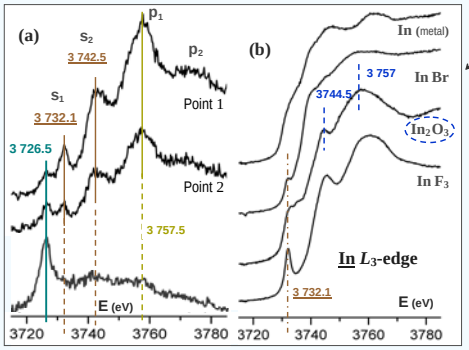


Fig. 8 - **In** L_3-edge *XANES* **spectra**
(a) points in ore sample LS 5-180.6
(b) model compounds.

Model compounds

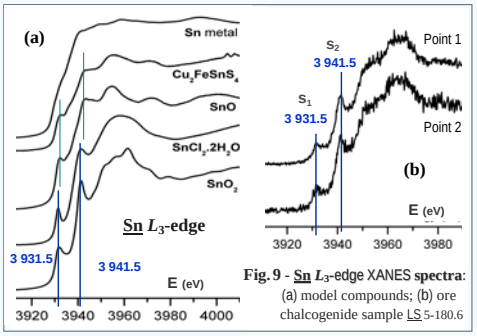


Fig. 9 - **Sn** L_3-edge XANES **spectra**:
(a) model compounds; (b) ore chalcogenide sample LS 5-180.6

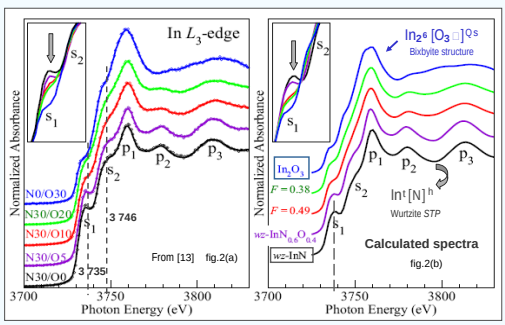


Fig. 10 - **In** L_3-edge *XANES* **spectra** of indium nitride and oxynitrides with wurtzite crystal structure-type [13]

In & Sn Crystal Chemistry: similarities & differences

Assigned in Transbaikalia as a *native metal* associated to lead [4], *indium* (Z=49) has the *electronic structure* [Kr] $4d^{10}\ 5s^2\ 5p^1$, and frequently assumes the *trivalent state*, thus suggesting the inertness of $5s^2$ electron-pair. With one more electron, *tin* (Z=50) has an electronic structure [Kr] $4d^{10}\ 5s^2\ 5p^2$, and *stable formal valences* (2+) and (4+). Contrary to tin that is largely widespread as an oxide (*cassiterite*), indium seldom forms specific minerals; *roquesite* ($CuInS_2$) was the first In-mineral to be described [5], followed by *indite* ($FeIn_2S_4$) - both with In in tetrahedral coordination by [S=] anions - and *dzhalindite*, $In(OH)_3$, with octahedral cations In^{3+} [6].

Excess-metal copper-rich "tetrahedral sulphides" may incorporate both In and Sn in diadochic replacement, as exemplified by the rare mineral *sakuraite*, $(Cu,Ag)_2(Zn,Fe)(In,Sn)S_4$ [7]. The synthesis of *excess-metal In-Se chalcogenides* [8] disclosed the occurrence of *polymetallic indium ions* – $[In_2]^{4+}$ *dimmers* and $[In_3]^{5+}$ *trimers* (fig.4). Conversely, metal-metal binding seems unfavorable for tin, as illustrated by the regular double tetrahedra $[Sn_2S_6]$ occurring in meso-structured semiconductor phases [9].

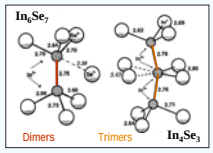


Fig. 4 – Reproduced from [8]

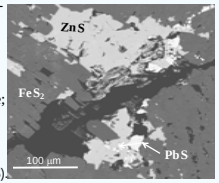
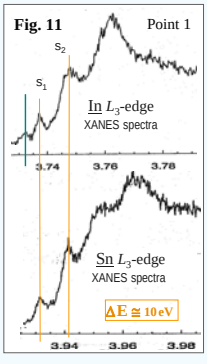


Fig. 6 - Photomicrograph from a polished section of ore sample LS 5-180.6
In black, a fissure; dark grey, pyrite (FeS_2); light grey, sphalerite (ZnS); white, galena (PbS).

Results

X-ray absorption spectra reflect the ***local symmetry*** and the ***chemical bonding*** of the absorbing element and the ***band character*** of the compound through the position of the *edge jump* and the *details* that follow.

L_3-edge XANES* spectra** collected by irradiating selected points (fig.7) in the ore sample (figs.8a & 9b) display ***two shoulders (s_1 & s_2, see fig.10 [13]) separated by ~10 eV (fig.11). Once In & Sn are both $4d^{10}$ elements, such details may indicate electronic transitions to unoccupied *d* states above the Fermi level, possibly 5*d* orbitals fivefold degenerated by the ligands [14]. Beyond these shoulders, a ***"white-line"*** [15] was observed at 3726.5 eV (fig.8a) and it constitutes the unique detail registered before the edge (3730 eV) in the In L_3-edge *XANES* spectrum collected at another point of the studied chalcogenide ore sample.



Final Comments

The *closest packing array* built up by $S^=$ *anions* in *tetrahedral sulphides* is particularly *suitable to house polymetallic ions by filling closely located interstitial sites* (fig.3). Once synthetic In-selenides display metal-metal bonding, it is not to exclude that *interactions may also occur between In-cations in natural chalcogenides*. This fact could account for the mentioned singularity of an extra *white line* present in the L_3-edge XANES spectra of In but not observed for Sn compounds [16].

The exact nature of this absorption detail is yet to be interpreted and further study of natural-plus-synthetic phases is in progress.

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